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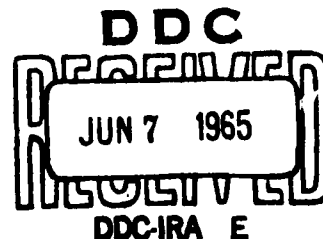
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TECHNICAL REPORT No. 43

Nitrogen-15 Magnetic Resonance Spectroscopy.

IV.   The Degenerate Bimolecular Exchange

of Protons in Ketimines

By Joseph B. Lambert and John D. Roberts

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Pasadena, California

May 1965

Nitrogen-15 Magnetic Resonance Spectroscopy. IV. The Degenerate Bimolecular Exchange of Protons in Ketimines[1,2]

Joseph B. Lambert,[3] Wallace L. Oliver,[4] and John D. Roberts

Contribution No. 3228 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California

Received

The imine protons of nitrogen-15 labeled ketimines exhibit temperature-dependent nuclear magnetic resonances. Analysis of the effect of concentration of substrate on the mean lifetime indicates that the spectral changes result from a bimolecular exchange of protons between imines. The activation energy of this process in

diphenylketimine-^{15}N was determined to be 13.8 ± 2 kcal./

mole, whereas in s-butylphenylketimine-^{15}N, the acti-

vation energy was about 6 kcal./mole. In the

latter case, separate resonances were observed for the

distinct syn and anti isomers.

Introduction

Nuclear magnetic resonance spectroscopy is ideally suited for

rate studies of rapidly reversible unimolecular reactions with

Arrhenius activation energies between 5 and 20 kcal./mole. Isomer-

ization processes,[5,6] ring inversions,[7,8] and valence tautomer-

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(5) H. S. Gutowsky and C. H. Holm, J. Chem. Phys., 25, 1228 (1956).

(6) L. H. Piette and W. A. Anderson, J. Chem. Phys., 30, 899 (1959).

(7) R. K. Harris and N. Sheppard, Proc. Chem. Soc., 1961, 418.

(8) F. A. L. Anet and J. S. Hartman, J. Am. Chem. Soc., 85, 1204 (1963).

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izations[9,10] have been studied by analysis of the temperature variation

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(9) M. Saunders, Tetrahedron Letters, No. 25, 1699 (1963).

(10) J. B. Lambert, Tetrahedron Letters, No. 27, 1901 (1963).

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of spectral parameters. Reactions of higher order involving proton

transfers have also been examined by means of spectral changes as a

function of solvent, pH, and solute concentration.[11] The rapid rates of

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(11) A. Loewenstein and T. M. Connor, Ber. Bunsenges.

Physik. Chem., 67, 280 (1963).

---

proton transfer reactions have often caused the spectral lineshapes to

be temperature insensitive.[12] Reversible changes with temperature

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(12) See, however, Z. Luz and S. Meiboom, J. Am. Chem.

Soc., 86, 4768 (1964); E. Grunwald, C. F. Jumper, and S. Meiboom,

ibid., 85, 522 (1963).

---

in the spectra of nitrogen-15 labeled ketimines are interpreted in the

following discussion in terms of an intermolecular exchange of protons

between nitrogen atoms.

Results and Discussion

In the absence of exchange, the proton on nitrogen in diphenyl-

ketimine-^{15}N (I) should be a doublet because of coupling with nitrogen-

$$^{15}N\overset{\displaystyle H}{\underset{\displaystyle \underset{C_6H_5}{\overset{\displaystyle C}{\diagup}}\diagdown C_6H_5}{\parallel}}$$

I
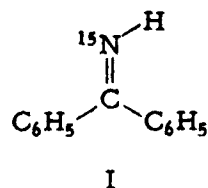
15. At 40°, however, the imine hydrogen resonance varies from a

single sharp peak in carbon disulfide or a broad singlet in carbon
tetrachloride and dimethyl sulfoxide, to no observable peak at all in
acetonitrile, deuterochloroform, and pentane. The spectrum of the
ketimine in 2-5% solutions of the last three solvents was examined to
-50°, at which temperature the solutions solidified. Whereas no
change occurred over this temperature range for the acetonitrile and
deuterochloroform solutions, the expected doublet appeared below 0°
in the spectrum of the pentane[13] solution (Figures 1a, b and 2). Under

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(13) The pentane had been treated with sulfuric acid for 2 days,
distilled, and dried over calcium hydride. The field increases from
left to right on all spectra.

---

identical conditions of solvent and temperature, the nitrogen-14
compound exhibited a single broad imine resonance which fell midway
between the two peaks of the nitrogen-15 compound (Figure 1c). The
integrated intensity of the two peaks, furthermore, was 1/10 that of
the phenyl peaks. There remains little doubt, therefore, that the
doublet resonance ($J_{15_{NH}}$ = 51.2 c.p.s.) arises from the imine proton
coupled with nitrogen-15.

This same phenomenon was observed at lower temperatures in
the spectrum of s-butylphenylketimine-^{15}N (II). At -60°, the imine
proton resonance consists of four peaks, which must arise from the
two distinct ketimine isomers (IIa and b) which are possible in this

IIa   IIb
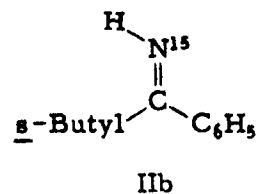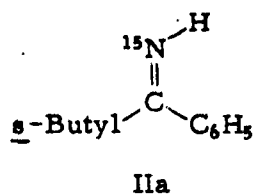
unsymmetrical system (Figure 3). The components of each small

doublet are chemically shifted about 11 c.p.s. from each other. The

low-field components in each doublet are separated by 50.6 c.p.s.,

and the high-field components are separated by 50.9 c.p.s. As the

temperature of the pentane solution is raised, the components of each

doublet broaden and finally coalesce (Figure 4, left side; only one of

the doublets is shown). The free-energy difference between isomers

was calculated to be 70 cal./mole from the equilibrium constant at

-60° (1.5, obtained by electronic integration).

The observation of separate geometric isomers of N-substi-

tuted imines has been claimed erroneously in the past.[14, 15] The

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(14) Oximes, semicarbazones, and N-haloimines are excluded

from consideration in this context.

(15) D. Y. Curtin and J. W. Hausser, *J. Am. Chem. Soc.*, 83,
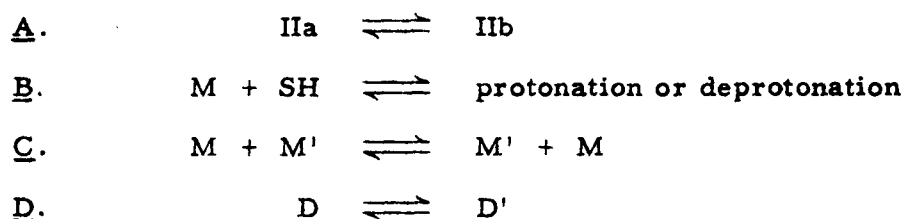
3474 (1961).

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actual isolation of both syn and anti forms of a given system was not

realized until quite recently, [16, 17] for the case of N-substituted

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(16) G. Saucy and L. H. Sternbach, *Helv. Chim. Acta*, 45,

2226 (1962).

(17) S. C. Bell, G. L. Conklin, and S. J. Childress, *J. Org. Chem.*, 29, 2368 (1964).

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benzophenone imines. The present observation of separate resonances for the two isomers of s-butylphenylketimine-^{15}N is the first example of cis-trans isomerism about a carbon–nitrogen double bond which is unsubstituted at nitrogen.

The coalescence of the peaks for the two isomers (Figure 4) results from a simple spin-exchange phenomenon. The possible mechanisms of exchange will be discussed in detail for the case of the unsymmetrical imine II.

A.		IIa $\rightleftharpoons$ IIb
B.	M + SH $\rightleftharpoons$	protonation or deprotonation
C.	M + M' $\rightleftharpoons$	M' + M
D.	D $\rightleftharpoons$	D'

Mechanism A involves a cis-trans isomerization. Mechanism B involves a proton exchange between monomer and some other species such as water or ammonia. Mechanism C is a special case of B, in which the second species is also monomer. Mechanism D involves a proton exchange within a dimeric structure.

In order to differentiate between the various mechanistic possibilities, the Gutowsky-Holm method[5, 18] was employed to determine

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(18) The author is indebted to Dr. S. Borčić for making available a Fortran program for calculation of line shapes as a function of the mean lifetime. The values of τ were determined by direct

comparison of observed and calculated spectra (Figure 4).

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mean lifetimes, τ, [19] which are related to the reaction rate in a manner

---

(19) The mean lifetime, τ, is defined as the time required for all but $1/e$ of the molecules to have reacted.

---

to be discussed. Figure 4 compares the calculated spectra with the observed spectra for various temperatures. The molecularity of the reaction must be determined before rates may be calculated from the mean lifetime.

Certain mechanistic possibilities may be eliminated by observing the effect on the mean lifetime of changes in reaction conditions. Addition of water directly to the solution of pentane had no effect on the mean lifetime. The presence of calcium hydride or calcium oxide in the n.m.r. tube had a similarly negligible effect. Mechanism B is thus eliminated, since addition or destruction of the most likely choices for SH, water and ammonia, do not affect the rate. When the concentration of ketimine was varied, however, significant changes in the mean lifetime were indicated by substantial line-shape changes. This excludes as the only mechanism any kind of unimolecular process, such as those represented in mechanisms A and D. Mechanism C therefore best accounts for the experimental details:

$$
\begin{array}{c}
\text{H} \diagdown \text{N} \\
\parallel \\
\text{R} \diagup \text{C} \diagdown \text{R}
\end{array}
\;+\;
\begin{array}{c}
\text{H}^* \diagdown \text{N}^* \\
\parallel \\
\text{R} \diagup \text{C} \diagdown \text{R}
\end{array}
\;\rightleftharpoons\;
\begin{array}{c}
\text{H}^* \diagdown \text{N} \\
\parallel \\
\text{R} \diagup \text{C} \diagdown \text{R}
\end{array}
\;+\;
\begin{array}{c}
\text{H} \diagdown \text{N}^* \\
\parallel \\
\text{R} \diagup \text{C} \diagdown \text{R}
\end{array}
$$

Such a pathway is bimolecular and degenerate; not only are both re-actants the same, but they are the same as the products.

Although the mechanism has been discussed in terms of a bimolecular process, the actual molecularity remains to be determined. The experimental facts could also be interpreted in terms of a termolecular process. The Gutowsky-Holm-Borčić treatment[5, 18] enables one to determine the mean lifetime, τ, which is simply the reciprocal of the first-order rate constant for a unimolecular process. The relationship is more complicated for reactions of higher order. The integrated form of the rate law given in

$$- \frac{dM}{dt} = kM^n \tag{1}$$

equation 1 is:

$$- \int_{M_0}^{M_0/e} M^{-n}\, dM = \int_{0}^{\tau} k\, dt$$

For $n = 1$:

$$k\tau = \ln \frac{M_0}{M_0/e} = \ln e = 1$$

In general, for $n \neq 1$:

$$k\tau = - \left[\frac{1}{-n+1}\, M^{-n+1} \right]_{M_0}^{M_0/e}$$

$$= \frac{1}{1-n}\left[M_0^{1-n} - \left(\frac{M_0}{e}\right)^{1-n} \right]$$

$$= M_0^{1-n}\left(\frac{1 - e^{n-1}}{1-n}\right) \tag{2}$$

Thus,
$$\log \tau = (1 - \underline{n}) \log \underline{M}_0 - \log \underline{k}' \qquad (3)$$

where
$$\frac{1}{\underline{k}'} = \frac{1}{\underline{k}} \left(\frac{1 - e^{\underline{n}-1}}{1 - \underline{n}} \right) = \tau \underline{M}_0^{\underline{n}-1}$$

A statistical factor of 2, which arises because two equivalent protons are exchanged in each reaction, is canceled by the spin factor which arises because exchange between nuclei of the same spin is not observed in the n.m.r. experiment.[11] From the slope of a plot of $\log \tau$ vs. $\log \underline{M}_0$, after equation 3, the molecularity was calculated to be about 1.7. Since the error in measuring the values of τ from calculated spectra is at least 10%, and the error in $\underline{M}_0$ is relatively large, this plot was deceptively linear, and the result must be judged accordingly. This analysis at least casts serious doubt on the presence of higher-order processes. A second-order process is most suitably accommodated by a transition state involving a concerted shift of two protons in a four-membered ring:
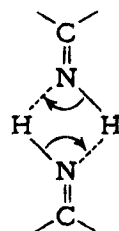

An admixture of a unimolecular process such as mechanism $\underline{D}$ cannot be excluded.

Arrhenius plots for the exchange reactions of I and II may be constructed from the rate constants calculated by equation 2 from machine-determined values of τ (Figures 5 and 6). The activation energy for the degenerate proton exchange in diphenylketimine is thus

calculated to be 13.8 ± 2 kcal./mole, and the values for s-butylphenyl-ketimine are 6.5 and 6.6 ± 2 kcal./mole. Two values arise since approach to the transition state can occur from either direction. The smaller value is necessarily associated with the less stable isomer. No imine hydrogen resonance was observed down to $-80°$ for di-n-butylketimine-^{15}N. The activation energy for exchange in systems containing two aliphatic substituents is therefore probably less than 5-7 kcal./mole. Sensitivity and solubility problems prevented accurate concentration studies of the proton exchange in I. It should be noted that the calculation of activation energies is completely independent of both the molecularity and the units of concentration, since changes in these quantities will not affect the slope of the plot. Therefore, the activation parameters are valid, even if the proposed mechanism of spin exchange is incorrect.

An isomerization process such as that depicted by mechanism A has been studied by Andreades[20] for the N-substituted imine III.

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(20) S. Andreades, J. Org. Chem., 27, 4157 (1962).

III
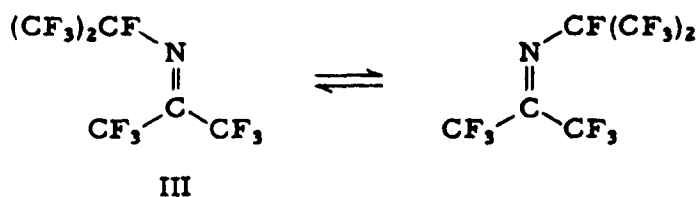
Analysis of the temperature dependence of the fluorine spectrum yielded an activation energy of 13 ± 3 kcal./mole. Replacement of the exchangeable imine proton with a methyl group in the ketimine systems

investigated in the present work might permit the observation of rotation about nonfluorinated carbon–nitrogen double bonds. Methyl-amine Schiff bases were therefore made from s-butyl phenyl ketone, n-propyl phenyl ketone, ethyl phenyl ketone, diisopropyl ketone, and p-chlorobenzophenone. In all cases but the first, the N–methyl reso-nances consisted of a single sharp peak, indicative of fast exchange, the coincidence of chemical shifts, or the presence of only a single isomer. This was particularly surprising for the methylimine of p-chlorobenzophenone, since Curtin and Hauser[16] reported that the N–methyl resonance consisted of two peaks. The N–methyl resonance of s-butylphenylketone methylimine (IV) was a doublet, the components

$$CH_3CH_2-CH(CH_3)-C(=N-CH_3)-C_6H_5$$
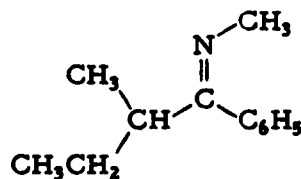
IV

of which were separated by 1 c.p.s. The invariance of the peak sepa-ration to a change of field from 14,100 to 23,500 gauss[21] identifies the

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(21) The author is indebted to Dr. Lois Durham, Stanford University, Stanford, California for recording the 100–Mc.p.s. spectra.

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doublet as a coupling, rather than a chemical shift. This is presuma-bly a five-bond coupling between the N–methyl protons and the methinyl proton of the s-butyl group.[22] The absence of chemically shifted

(22) G. J. Karabatsos, R. A. Taller, and F. M. Vane, Tetrahedron Letters, No. 18, 1081 (1964).

N-methyl resonances for all members of this series renders impossible the study of isomerization about the carbon-nitrogen double bond by n. m. r. methods.[23]

(23) There is a formal structural analogy between the bimolecular exchange of imine protons in the present study, and the exchange of hydrogen-bonded protons in base pairs in DNA to form abnormal tautomers. Since these tautomers are capable of forming hydrogen bonds with the incorrect bases, e. g., A—C, G—T, it has been suggested that they give rise to mutations by perturbing the genetic code, cf., P. -O. Löwdin, "Electronic Aspects of Biochemistry, " B. Pullman, ed., Academic Press, Inc., New York, 1964, pp. 167 f.

Experimental

Melting points and boiling points are uncorrected. Melting points were measured on either the Büchi or the Hershberg apparatus. Proton magnetic resonance spectra were measured on the Varian Associates Model A-60 spectrometer operated at 60. 0 Mc. p. s. and 14, 100 gauss. The authors would like to thank Drs. S. L. Manatt and D. D. Elleman of the Jet Propulsion Laboratory, Pasadena, California, for the use of a temperature-adaptable A-60.

Benzamide-^{15}N. — A 100-ml. three-necked round-bottomed
flask was equipped with an inlet tube for dry nitrogen, a dropping
funnel, and a reflux condenser leading through two potassium hy-
droxide drying tubes to a second flask. The latter 200-ml. round-
bottomed flask was equipped with the inlet tube, a mechanical stirrer,
and an exit tube which led through a trap to a 10% hydrochloric acid
solution. After nitrogen flow was initiated, the second flask was
flamed out several times and filled with 4.38 g. (0.0312 mole) of
benzoyl chloride and 120 ml. of anhydrous ether. The stirred ether
solution was cooled in a Dry Ice-acetone bath, and ammonia was
introduced slowly. The ammonia was generated in the first flask by
the dropwise addition of 3 g. (0.0550 mole) of concentrated aqueous
ammonium-^{15}N chloride (Merck Sharpe and Dohme of Canada) to a
refluxing solution of 5.7 g. of sodium hydroxide in 14 ml. of water.
An hour and a half after evolution of ammonia had ceased, the second
flask was warmed to room temperature and allowed to stand for 12 hrs.
There was no ammonia trapped in the hydrochloric acid solution. The
ether solution was filtered, and the solid was washed with five 18-ml.
portions of absolute ethanol. The filtrate was concentrated to incipi-
ent crystallization by rotary evaporation, and 75 ml. of benzene was
added. The solution was filtered at its boiling point, and the residue
was washed with three 35-ml. portions of hot benzene. Two crops of
benzamide, totaling 1.582 g., were obtained from this solution. The
original solid by-product was washed with acetone. This solution
eventually produced an additional 1.428 g. of the product. The total
yield of benzamide-^{15}N was 3.010 g. (0.0246 mole, 89.5%), m.p.
122.8-123.2° (reported 121-123°).[24] The excess ammonium chloride

(24) A. Murray, III, and D. L. Williams, "Organic Syntheses with Isotopes," Part II, Interscience Publishers, Inc., New York, 1958, p. 1726.

(1.58 g.) was recovered quantitatively.

Benzonitrile-^{15}N. — Benzamide-^{15}N (1.582 g., 0.0130 mole) and sodium aluminum chloride (2.50 g., 0.0130 mole) were mixed carefully in a 50-ml. round-bottomed flask equipped with a distillation head. The mixture was heated in a silicone oil bath at 180° until effervescence ceased. Heating was continued with a free flame until distillation of the product was finished. The yield of benzonitrile-^{15}N was 0.995 g. (0.00956 mole, 73.5%).

Diphenylketimine-^{15}N. — Phenyl Grignard reagent was prepared from 3.16 g. (0.0201 mole) of bromobenzene and 0.500 g. (0.0206 mole) of magnesium in 30 ml. of anhydrous ether contained in a 100-ml. three-necked round-bottomed flask equipped with a dropping funnel and a reflux condenser. Benzonitrile-^{15}N (1.87 g., 0.0180 mole) in 10 ml. of anhydrous ether was added dropwise at room temperature, and the mixture was mechanically stirred for 7.5 hrs. The solution was cooled, and 3.61 g. of anhydrous methanol was added carefully at room temperature. The resulting gum was stirred for 30 min. until it became completely crystalline. The slurry was filtered, and the ether and excess methanol were removed by distillation. The residue on distillation gave 2.16 g. (0.0121 mole, 67.2%) of diphenylketimine-^{15}N, b.p. 120° (1 mm.), n_D^{37} = 1.6088.[25]

(25) P. L. Pickard and T. L. Tolbert, J. Org. Chem., 26, 4886 (1961).

Diphenylketimine-¹⁵N Hydrochloride. — A 200-ml. three-necked round-bottomed flask was flamed out and filled with 0.681 g. (0.00380 mole) of diphenylketimine-¹⁵N and 80 ml. of diethyl ether which had just been distilled from lithium aluminum hydride. A nitrogen atmosphere was maintained in the flask throughout the reaction. Hydrogen chloride gas was bubbled through a sulfuric acid trap into the ether solution until no more precipitate formed. The solid was isolated by filtration and dried under vacuum in a desiccator. The yield of diphenylketimine-¹⁵N hydrochloride was 0.643 g. (0.00298 mole, 78.4%).

s-Butylphenylketimine-¹⁵N was prepared in the same manner as diphenylketimine-¹⁵N (vide supra) from 4.50 g. (0.0328 mole) of s-butyl bromide, 0.77 g. (0.0140 mole) of magnesium, 1.60 g. (0.0154 mole) of benzonitrile-¹⁵N, and 3.8 g. of anhydrous methanol. The yield of ketimine (1.689 g., 0.0104 mole) was 74.3%.

Potassium cyanide-¹⁵N was obtained from Volk Radiochemical Laboratories.

n-Butyl Cyanide-¹⁵N. — n-Butyl chloride was added dropwise over a period of 40 min. to a solution of 1.09 g. (0.0165 mole) of potassium cyanide-¹⁵N and 1.0 g. of sodium acetate in dimethyl sulfoxide heated at 120° in a 100-ml. three-necked round-bottomed flask equipped with a thermometer, reflux condenser, and dropping funnel. After the solution had refluxed for 18 hrs., water was added,

and the nitrile was removed by extraction with three portions of diethyl ether. Hydrochloric acid was added to hydrolyze any iso-cyanate that might have been present, and the solution was again extracted with ether. The ether was removed by distillation, and the product was dried over calcium chloride and phosphorus pentoxide. The yield of n-butyl cyanide-^{15}N (valeronitrile-^{15}N) was 1.007 g. (0.0120 mole, 72.7%).[26]

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(26) L. Friedman and H. Shechter, J. Org. Chem., 25, 877 (1960).


Di-n-butylketimine-^{15}N was prepared in the same manner as diphenylketimine-^{15}N (vide supra) from 3.0 g. (0.0219 mole) of n-butyl bromide, 0.50 g. (0.00910 mole) of magnesium, 1.007 g. (0.0120 mole) of n-butyl cyanide-^{15}N, and 3.2 g. of anhydrous methanol. The yield of ketimine (0.533 g., 0.00375 mole) was 41.2%.

s-Butyl phenyl ketone. — A 1-l. three-necked round-bottomed flask equipped with a gas-inlet tube, a reflux condenser, and a dropping funnel was flamed out and flushed with argon. Benzonitrile (40 g., 0.388 mole) was added dropwise with stirring to a Grignard reagent formed from 68.5 g. (0.500 mole) of s-butyl bromide and 12.4 g. (0.510 mole) of magnesium in 500 ml. of anhydrous ether. The yellow-gray mixture was refluxed for 12 hrs. After the mixture had cooled to room temperature, 96 g. of methanol was added very slowly with agitation. The precipitate was removed by filtration when it had become completely crystalline. Methanol (100 ml.) containing 10 ml. of water was added, and the solution was allowed to stand for

an hour. The ether and methanol were removed by distillation at atmospheric pressure, and the residue was fractionated at 5 mm. After benzonitrile was removed at 72-3°, two fractions (94-7°, 97-100°) of ketone-ketimine were collected. The mixtures were treated with water until VPC traces showed no ketimine to be present.

N-Methyl-s-butylphenylketimine. — The crude s-butyl phenyl ketone (5 g.) prepared as described above was placed in a 15-ml. heavy-walled ampoule and degassed three times at 0.1 mm. to remove all traces of ammonia. Methylamine (1 g.), prepared by the addition of potassium hydroxide solution to the stock 40% aqueous solution, was distilled under vacuum into the ampoule, which was sealed at atmospheric pressure and heated at 175° for 3 days. An aqueous layer separated. The tube was opened, the water was removed, and four additional milliliters of amine were distilled under vacuum into the tube, which was again sealed and heated at 175° for 1 day. No further reaction was evident, so the tube was opened and the contents distilled, b.p. 67° (1 mm.). VPC analysis showed the distillate to contain about 60% ketimine and 40% ketone. Pure samples of the former were obtained by preparative vapor phase chromatography.
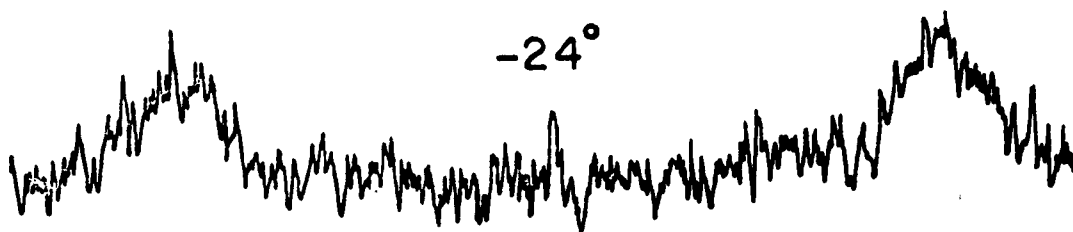
Fig. 1. -- Proton spectrum of diphenylketimine, -40°.

c

b

a

10.0   8.0   6.0
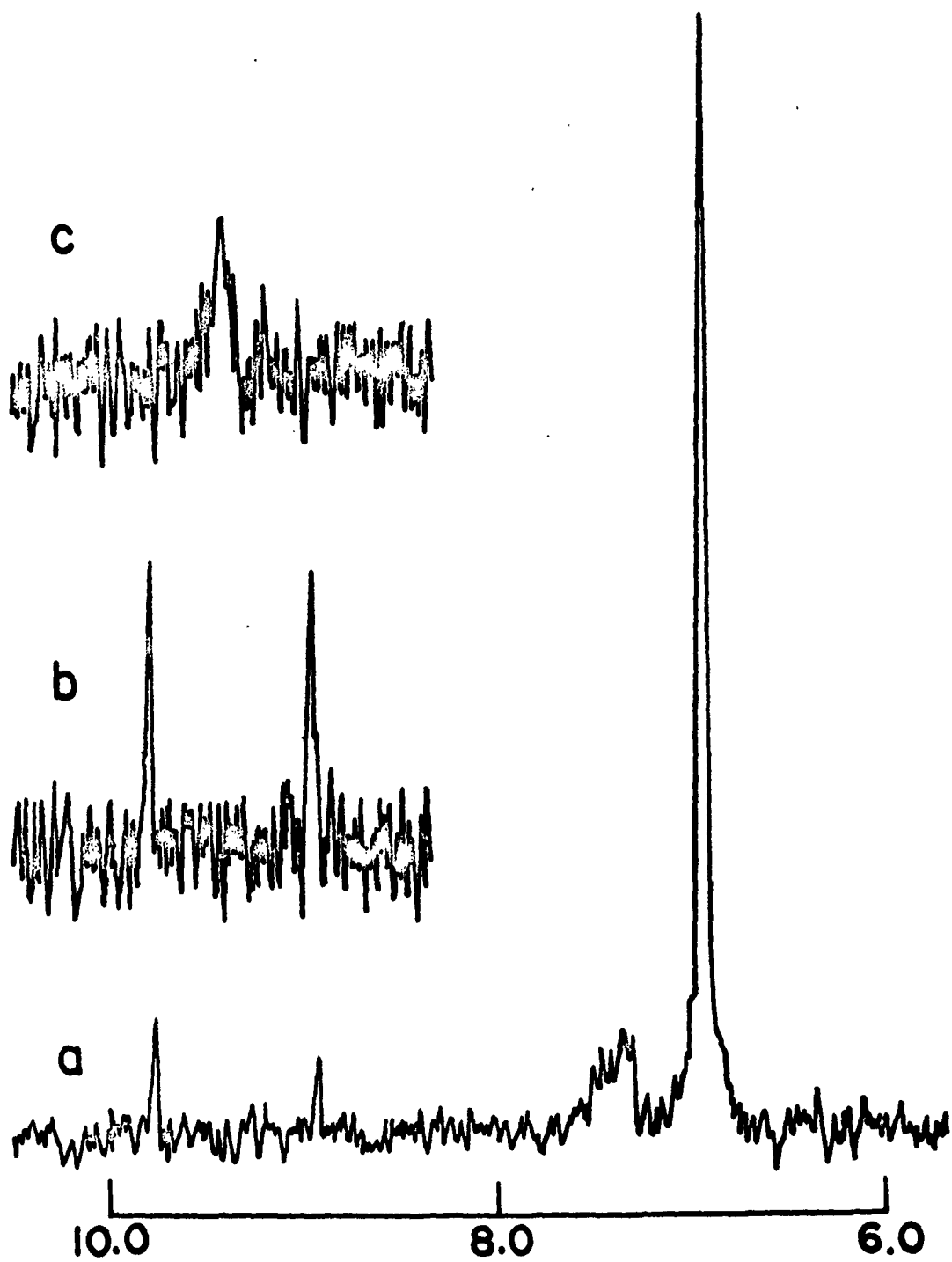
Fig. 2. -- Temperature dependence of the imine proton
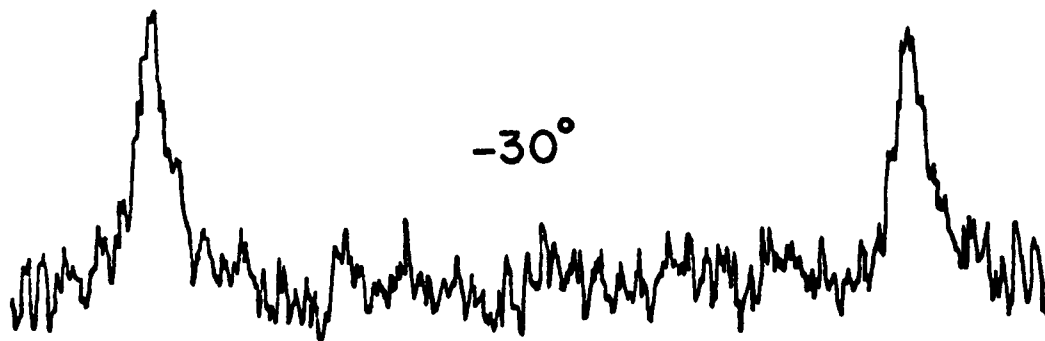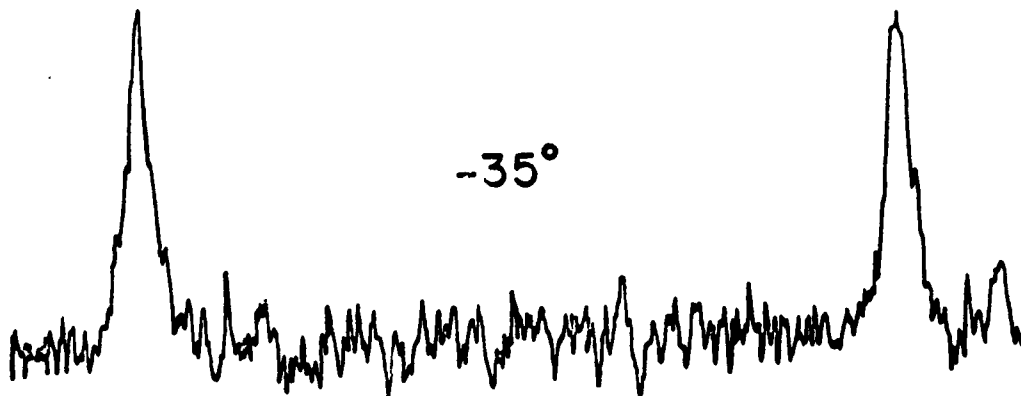
resonance in diphenylketimine-^{15}N.

-14°

-24°

-30°

-35°

⊢—— 25 cps ——⊣

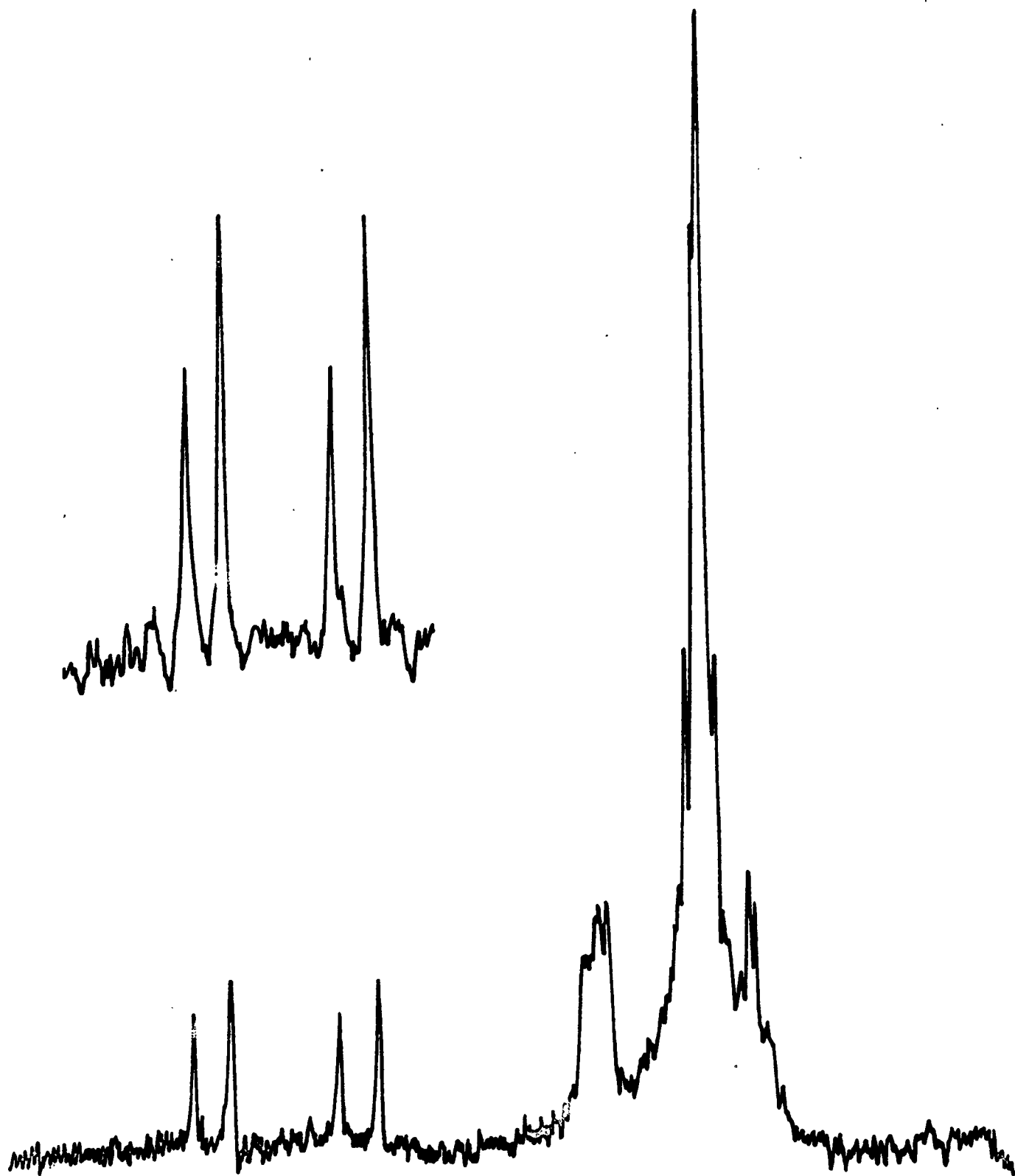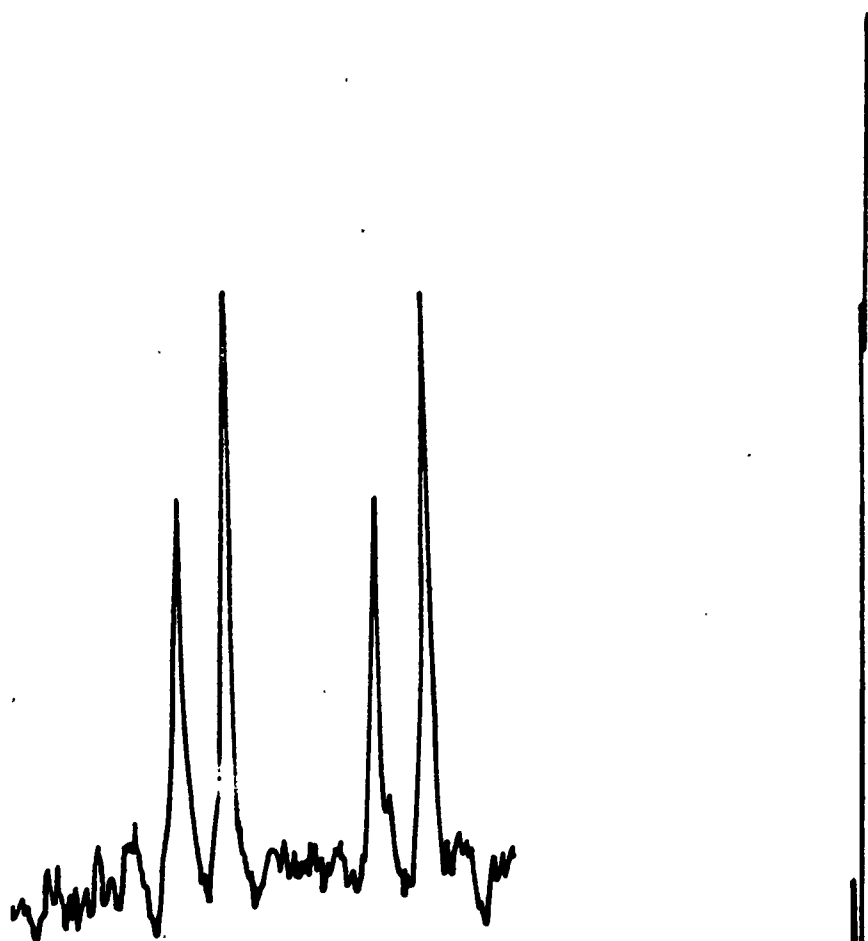Fig. 3. -- Proton spectrum of _s_-butylphenylketimine-^{15}N, -60°.

Fig. 4. — Temperature dependence of the imine proton resonance

   of s-butylphenylketimine-^{15}N. The calculated curves

   were derived from p_A (-60°) = 0.39, p_B (-60°) = 0.61,

   T_2 = 1.89 sec. and δ (slow exchange) = 11.0 c.p.s. The

   populations were corrected for changes with temperature

   (ΔF = 70 cal.). The τ_A values which correspond to the

   calculated curves are (top to bottom): 0.040, 0.055,

   0.075, 0.095, 0.130, and 0.250 sec., respectively. The

   bottom curve corresponds to the slow-exchange limit

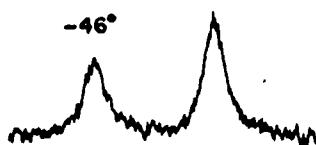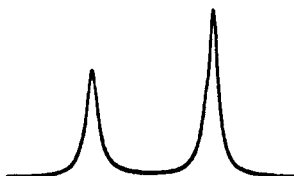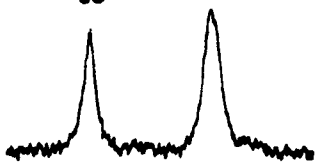   ($\tau_A \geq 1.0$).

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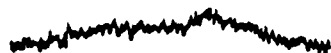
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|←—11.0 cps—→|

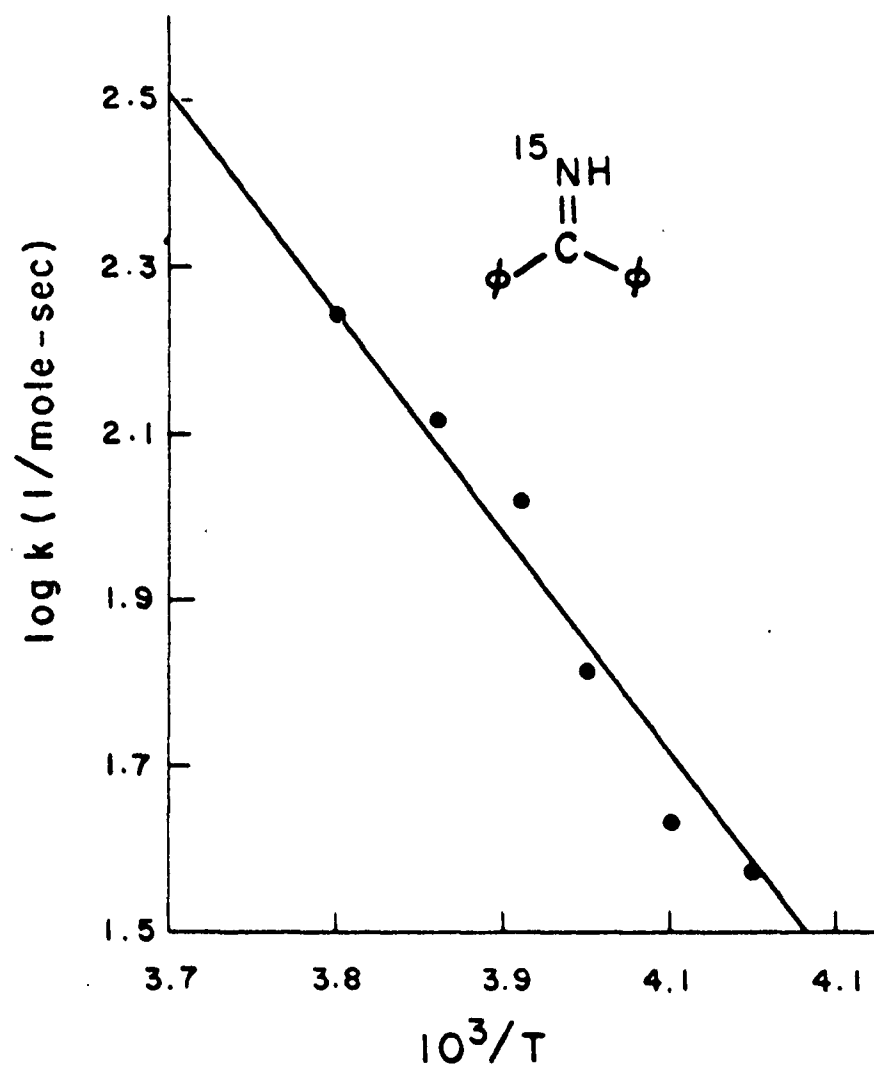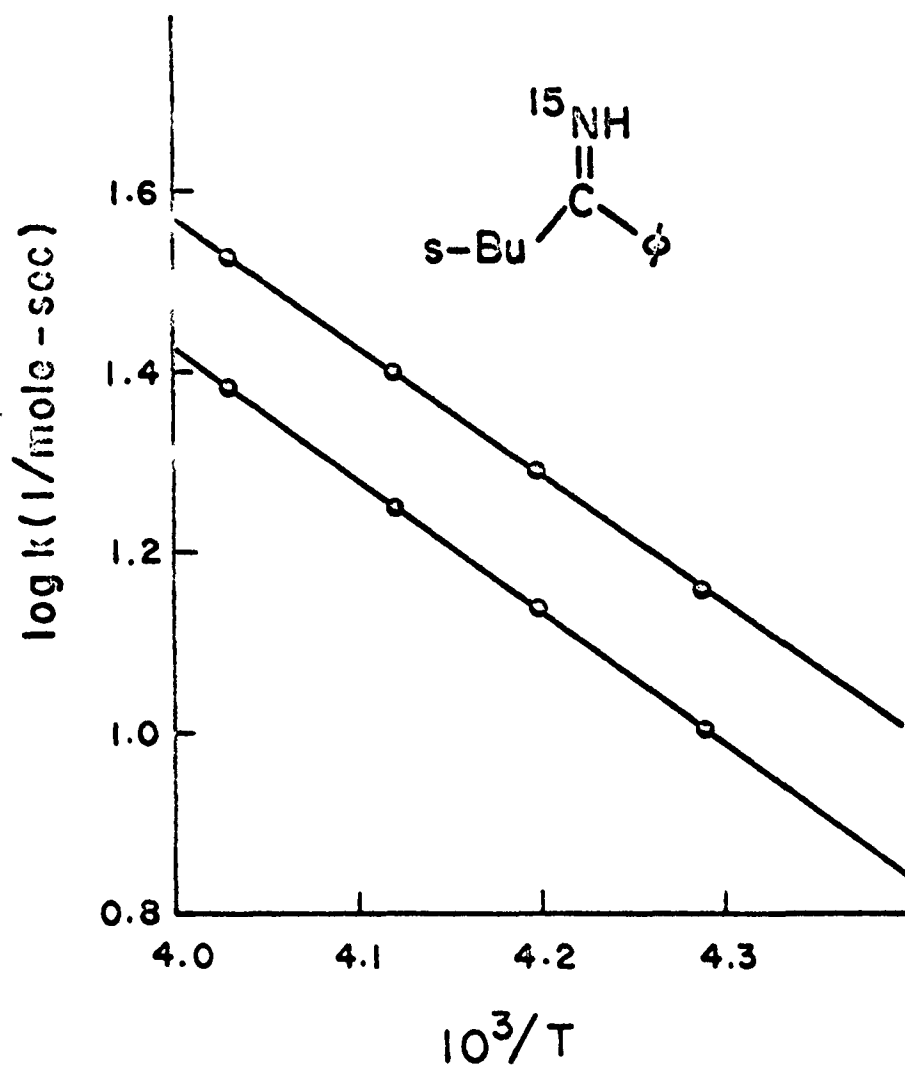Fig. 5. -- Arrhenius plot for diphenylketimine-[15]N.

Fig. 6.-- Arrhenius plot for s-butylphenylketimine-^{15}N.

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The imine protons of nitrogen-15 labeled ketimines exhibit temperature-dependent nuclear magnetic resonances. Analysis of the effect of concentration of substrate on the mean lifetime indicates that the spectral changes result from a bimolecular exchange of protons between imines. The activation energy of this process in diphenylketimine-^{15}N was determined to be 13.8 ± 2 kcal/mole, whereas in s-butylphenylketimine-^{15}N, the activation energy was about 6 kcal/mole. In the latter case, separate resonances were observed for the distinct <u>syn</u> and <u>anti</u> isomers.

14. KEY WORDS	LINK A		LINK B		LINK C	
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